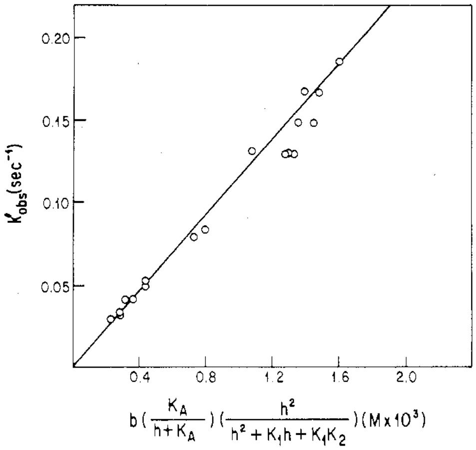

Figure 3. Linear plot of rate data for CO_2 uptake by Co(tetren)(OH)$^{2+}$ at 20 °C and $I = 0.5$ M (NaCl).

mental temperatures are given in Table I. The alternative procedure, given enough data (as is true at 20 °C), is to plot $k'_{obsd} = k_{obsd} - k_1([H^+]/[H^+] + K_c)$ vs. $b(K_A/[H^+] + K_A)\cdot([H^+]^2/[H^+]^2 + K_1[H^+] + K_1K_2)$, which should yield a straight line through the origin of slope k_2. Such a plot is presented in Figure 3, and a least-squares analysis gives an intercept indistinguishable from zero (0.006 ± 0.053) and a slope of $k_2 = 113 \pm 4$ M^{-1} s^{-1}. This latter figure is in excellent agreement with the "average" value of $k_2 = 115 \pm 9$ M^{-1} s^{-1} already determined at 20 °C and recorded in Table I, along with the data at the other temperatures and the activation parameters calculated therefrom. One notes that these parameters are barely distinguisable from the corresponding figures[4] for Co(NH$_3$)$_5$OH^{2+}, for which $k_2 = 220$ M^{-1} s^{-1} at 25 °C, $\Delta H_2^{\ddagger} = 15.3 \pm 0.9$ kcal mol^{-1}, and $\Delta S_2^{\ddagger} = 3.6 \pm 3.0$ cal deg^{-1} mol^{-1}. In fact, most of the diaquotetraamine-cobalt(III) complexes also have rate parameters rather similar to these, with slight differences seemingly related to differences in the pK_A values of the various aquo species.[16] Since the pK_A's for Co(tetren)(OH$_2$)$^{3+}$ (6.3, as measured above) and for Co(NH$_3$)$_5$(OH$_2$)$^{3+}$ (6.6[4]) differ but little, no significant contrasts in carbon dioxide uptake kinetics are to be expected, as confirmed herewith.

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Registry No. $\alpha\beta S$-[Co(tetren)(CO$_3$)]ClO$_4$, 67772-78-5; $\alpha\beta S$-Co(tetren)(CO$_3$)$^+$, 67738-27-6; $\alpha\beta S$-Co(tetren)(OH$_2$)$^{3+}$, 67738-28-7; $\alpha\beta S$-[Co(tetren)(OH)](ClO$_4$)$_2$, 67738-30-1; H$^+$, 12408-02-5.

References and Notes

(1) (a) Presented in part at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974; see Abstracts, No. INORG 113. (b) Previous paper in this series: G. M. Harris and K. E. Hyde, *Inorg. Chem.*, **17**, 1892 (1978).
(2) T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **90**, 6360 (1968).
(3) D. A. Palmer and G. M. Harris, *Inorg. Chem.*, **13**, 965 (1974).
(4) E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Am. Chem. Soc.*, **95**, 4169 (1973).
(5) T. P. Dasgupta, *Inorg. Chim. Acta*, **20**, 33 (1976).
(6) K. E. Hyde, G. H. Fairchild, and G. M. Harris, *Inorg. Chem.*, **15**, 2631 (1976).
(7) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 2097 (1966).
(8) D. A. House and C. S. Garner, *Inorg. Chem.*, **6**, 272 (1967).
(9) These complexes are wrongly characterized by House and Garner as α isomers. Later Snow, Marzilli, and Sargeson showed on the basis of crystallographic data that α-hydroxo(tetraethylenepentamine)cobalt(III) ion prepared by base hydrolysis of $\alpha\beta$-chloro(tetraethylenepentamine) ion is in fact ($\alpha\beta S$)-hydroxo(tetraethylenepentamine)cobalt(III) ion: M. R. Snow, D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Chem. Commun.* 891 (1969); M. R. Snow, *J. Chem. Soc., Dalton Trans.*, 1627 (1972).
(10) Instranal Laboratory, Inc. Rensselaer, N.Y. 12144.
(11) K. Nakamoto, "Infra-red Spectra of Inorganic Co-ordination Compounds", Wiley, New York, N.Y. 1970, p 170.
(12) The extinction coefficient of ($\alpha\beta S$)-carbonato(tetraethylenepentamine)cobalt(III) ion at 490 nm is 195, whereas that of the corresponding aquo complex is 109.
(13) The extinction coefficient of ($\alpha\beta S$)-carbonato(tetraethylenepentamine)cobalt(III) ion at 500 nm is 198, whereas that of the corresponding hydroxo complex is 140.
(14) P. J. Elving, J. M. Markowitz, and I. Rosenthal, *Anal. Chem.*, **28**, 1179 (1956).
(15) See footnote 19 of ref 4 for this update of our initially published values for the rate parameters for Co(NH$_3$)$_5$(CO$_3$)$^+$ decarboxylation.[2]
(16) T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **99**, 2490 (1977).

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Oxidation of Hydrazine by Iodine in Aqueous Perchloric Acid

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The oxidation of aqueous hydrazine by iodine solutions is a well-known reaction that has been used as a basis for the iodometric determination of hydrazine.[1] The kinetics have been repeatedly studied with conflicting results, particularly in the [I$^-$] dependence of the rate law: Berthoud and Perrot[2] report an inverse second-order dependence of the rate law on [I$^-$] in chloride media, [I$^-$] = 0.05–0.20 M; in hydrogen sulfate media, Arora et al.,[3] in [I$^-$] = 0.008–0.046 M, Sen Gupta and Sen Gupta,[4] in [I$^-$] = 0.011–0.046 M, and Hasty,[5] in [I$^-$] = 0.02–0.12 M, all report different, complex inverse dependences on [I$^-$]. Hasty's work, while more recent, exhibits large experimental scatter, large uncertainties in his derived rate parameters, and a complex hydrogen ion dependence that is not substantiated by his published data. To resolve these discrepancies we undertook an investigation of this reaction in constant ionic strength, noncomplexing perchlorate media at 25 °C.[6] We report here the conclusions of this study which establish a well-defined rate law.

Experimental Section

Reagents. All solutions were prepared with water redistilled from alkaline permanganate. Sodium perchlorate and sodium iodide were recrystallized from redistilled water, and stock NaI solutions were stored under N$_2$ in brown bottles in the dark. Iodine solutions were prepared by dissolving resublimed I$_2$ in dilute NaI containing a trace of dilute HClO$_4$ to inhibit I$_2$ hydrolysis and were stored similarly. Hydrazinium perchlorate was prepared as described previously.[7] Perchloric acid was doubly distilled, and other reagents were of analytical quality.

Stoichiometry. The stoichiometry[1,6] was reconfirmed over the pH range 1.5–9.0 using HClO$_4$ and acetate, phosphate, and borate buffers. The ratio $\Delta[I_2]/\Delta[N_2H_5^+]$ was found to be 2.01 ± 0.02, consistent with eq 1 in the acidic media.

$$2I_2 + N_2H_5^+ \rightarrow N_2 + 4I^- + 5H^+ \qquad (1)$$

Kinetics. Runs were performed by flooding with I$^-$, H$^+$, and N$_2$H$_5^+$, at 25 °C and at $\mu = 0.35$ M, maintained with NaClO$_4$, unless otherwise noted. Kinetic solutions were deoxygenated with a stream of N$_2$ prior to addition of the I$_2$ solution, and kinetics were followed continuously in a thermostated spectrophotometer at λ 467 nm, an isosbestic point of the I$_2$–I$_3^-$ system, at which other species in the mixture are essentially transparent. The ln $(A_t - A_\infty)$ vs. time data were linear over at least 2 half-lives and the pseudo-first-order rate parameters $k_{obsd} = -d \ln (A_t - A_\infty)/dt$ were independent of initial [I$_2$].

Results and Discussion

The k_{obsd} values were proportional to [N$_2$H$_5^+$] and inversely proportional to [H$^+$], as shown by the constancy of $k' = {}^1/_2k_{obsd}[H^+]/[N_2H_5^+]$ at [I$^-$] = 0.102 ± 0.001 M. For

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Table I. Dependence of k_{obsd} on $[\text{I}^-]$ [a]

$[\text{I}^-]/\text{M}$	$10^4k_{\text{obsd}}/\text{s}^{-1}$	$10^4k_{\text{calcd}}/\text{s}^{-1}$
0.0208	24.4[b]	24.1
0.0414	9.8	10.4
0.0614	6.3[b]	6.13
0.101	2.94[b]	2.95
0.121	2.19	2.23
0.141	1.78	1.74
0.163	1.42[b]	1.37
0.182	1.07	1.14
0.202	0.96	0.96

[a] 25 °C, $\mu = 0.35$ M (NaClO_4), $[\text{H}^+] = 0.101$ M, $[\text{N}_2\text{H}_5^+] = 0.0168$ M. [b] Average of two determinations.

$[\text{H}^+]/\text{M}$, $[\text{N}_2\text{H}_5^+]/\text{M}$ and $10^4k'/\text{s}^{-1}$ the following values were obtained: 0.199, 0.0168, 9.3; 0.101, 0.0168, 8.85 ± 0.35; 0.0617, 0.0168, 9.1; 0.102, 0.0218, 8.5; 0.100, 0.0101, 8.4; 0.100, 0.00839, 8.85 ± 0.05. These results are consistent with previous studies in dilute acids[2,4] and are inconsistent with Hasty's proposed complex $[\text{H}^+]$ dependence of the rate law, eq 2. No evidence of a $[\text{H}^+]$-independent term, A, was found

$$R = \frac{[\Sigma\text{N}_2\text{H}_5^+][\Sigma\text{I}_2]}{(1 + Q_1[\text{I}^-])}\left\{A + \frac{B}{[\text{H}^+][\text{I}^-]}\right\} \qquad (2)$$

at $[\text{I}^-] = 0.102$ M; with use of Hasty's rate parameters, the $[\text{H}^+]$-independent term should have predominated under the above conditions with the ratio $A[\text{H}^+][\text{I}^-]/B$ ranging from 6 to 19. We conclude there is no evidence for a $[\text{H}^+]$-independent term.

The effect of ionic strength on k' at $[\text{I}^-] = 0.0414$, $[\text{N}_2\text{H}_5^+] = 0.0169$, and $[\text{H}^+] = 0.0420$ M was minimal. For μ/M and $10^3k'/\text{s}^{-1}$ respectively the following values were obtained: 0.101, 2.82; 0.281, 2.89; 0.461, 2.59; 0.641, 2.15; 0.821, 1.78. For the range $\mu = 0.10$–0.40 M in ClO_4^- media, k' is not significantly dependent on μ. In the presence of methanol, 0.65 M, or air-saturated kinetic solutions, k_{obsd} values were depressed 10%. Substitution of NaCl, $[\text{Cl}^-] = 0.17$ M, or NaHSO_4, $F_{\text{HSO}_4^-} = 0.064$ M, had no significant effect on k_{obsd}. In the case of the NaHSO_4 substitution, $[\text{H}^+]$ and μ were maintained ($\mu = 0.35$ M) with HClO_4 and NaClO_4, using $Q_{\text{HSO}_4^-} = 0.042$ M for the dissociation quotient of HSO_4^-.[9]

In determining the $[\text{I}^-]$ dependence of k_{obsd}, account was taken of the well-established formation quotient of I_3^-, $Q_1 = 725\ \text{M}^{-1}$.[8] In no case did the calculated free $[\text{I}^-]$ differ from the total, analytical iodide, F_{I^-}, by more than 4%. The k_{obsd} were found to have a complex, inverse dependence on $[\text{I}^-]$, qualitatively consistent both with the reported $1/[\text{I}^-]^2$ dependence at $[\text{I}^-] > 0.1$ M[2,5] and with the $1/(1 + b[\text{I}^-])$ dependence at $[\text{I}^-] < 0.04$ M.[4,5] Two fits of the data were compared,[10] eq 3 and 4. Equation 3 fits the data significantly

$$k' = a/(1 + b[\text{I}^-] + c[\text{I}^-]^2) \qquad (3)$$

$$k' = (A + (B/[\text{I}^-]))(1 + Q_1[\text{I}^-])^{-1} \qquad (4)$$

better than eq 4: with b constrained ($b = Q_1 = 725\ \text{M}^{-1}$), $a = 0.148 \pm 0.006\ \text{s}^{-1}$ and $10^{-3}c = 9.1 \pm 0.9\ \text{M}^{-2}$. The average percent deviation is 3% and the maximum, 6.5%. Using eq 4, $10^2A = 3.35 \pm 0.29\ \text{s}^{-1}$ and $10^3B = 2.61 \pm 0.35\ \text{M s}^{-1}$, with an average percent deviation of 12% and a maximum of 35%.

Mechanistically eq 3 is consistent with the involvement of I^-, both in nonproductive preequilibria and in steady-state production of intermediates. Two preequilibria were considered: the ionic species I_4^{2-} has been reported in the solid state[11] and has been proposed as a transition state in the I^-, I_3^- exchange.[12] However, the apparent kinetic Q_2, $c/b = 12.6 \pm 0.6\ \text{M}^{-1}$ from eq 3, is much larger than the value of 0.184 M^{-1} estimated by Effenberger[13] in 2 M NaNO_3 and is also inconsistent with the $[\text{I}^-]$ dependence of the solubility of I_2,[8] upon which the value of Q_1 is based. Alternatively, no evidence for the species $\text{N}_2\text{H}_5\text{I}$ was found. The UV spectrum of I^- (λ_{max}/nm 224, 195) was independent of $[\text{N}_2\text{H}_5^+]$, 0–0.29 M, in mixed (Na^+, N_2H_5^+) ClO_4^- media; and the solubility of $\text{N}_2\text{H}_5^+\text{HSO}_4^-$ was independent of $[\text{I}^-]$, 0–0.25 M, in mixed $\text{Na}^+(\text{ClO}_4^-, \text{I}^-)$ media. We conclude that preequilibrium involvement of I^- with I_3^- or with N_2H_5^+ does not account for the observed $[\text{I}^-]$ dependence of the rate law.

However, the steady-state mechanism, eq 5 and 6, coupled

$$\text{I}_2 + \text{N}_2\text{H}_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{N}_2\text{H}_4\text{I}^+ + \text{I}^- \qquad (5)$$

$$\text{N}_2\text{H}_4\text{I}^+ \xrightarrow{k_2} \text{products} \qquad (6)$$

with the rapid equilibria, eq 7 and 8, yield the rate law, eq

$$\text{I}_2 + \text{I}^- \rightleftarrows \text{I}_3^- \qquad Q_1 = 725\ \text{M}^{-1} \qquad (7)$$

$$\text{N}_2\text{H}_5^+ \rightleftarrows \text{N}_2\text{H}_4 + \text{H}^+ \qquad Q_\text{a} = 3 \times 10^{-9}\ \text{M} \qquad (8)$$

9:

$$R = -(1/2)\frac{\text{d}F_{\text{I}_2}}{\text{d}t} = k_1Q_\text{a}F_{\text{I}_2}F_{\text{N}_2\text{H}_5^+}/[\text{H}^+](1 + Q_1[\text{I}^-])\left(1 + \frac{k_{-1}}{k_2}[\text{I}^-]\right)$$

or

$$k_{\text{obsd}} = 2k_1Q_\text{a}F_{\text{N}_2\text{H}_5^+}/[\text{H}^+](1 + Q_1[\text{I}^-])\left(1 + \frac{k_{-1}}{k_2}[\text{I}^-]\right) \qquad (9)$$

The k_{obsd}–$[\text{I}^-]$ data were fit using a weighted, least-squares program, constraining $Q_1 = 725\ \text{M}^{-1}$; the optimized values obtained are $k_1Q_\text{a} = 0.145 \pm 0.005\ \text{s}^{-1}$ and $k_{-1}/k_2 = 12.0 \pm 0.5\ \text{M}^{-1}$. The k_{calcd} values are shown in Table I; the average percent deviation is 2.8% and the maximum is 6.5%. Taking $Q_\text{a} = 3 \times 10^{-9}$ M, the second-order rate constant, k_1, is $4.4 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$, substantially less than that observed for diffusion-controlled reactions. We conclude that the observed rate law is consistent with the formation of a steady-state iodine–hydrazine intermediate, formulated as $\text{N}_2\text{H}_4\text{I}^+$, which is formally composed of 1 mol each of N_2H_4 and of I^+.

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Registry No. N_2H_5^+, 18500-32-8; I_2, 7553-56-2; I^-, 20461-54-5.

References and Notes

(1) J. N. Cooper and R. W. Ramette, *J. Chem. Educ.*, **46**, 872 (1969).
(2) A. Berthoud and D. Perrot, *Helv. Chim. Acta*, **17**, 32 (1934).
(3) R. Arora, S. Harmalka, and E. Singh, *Z. Phys. Chem. (Leipzig)*, **221**, 297 (1962).
(4) K. Sen Gupta and S. Sen Gupta, *Z. Phys. Chem. (Frankfurt am Main)*, **45**, 378 (1965).
(5) R. Hasty, *Z. Phys. Chem. (Frankfurt am Main)*, **94**, 53 (1975).
(6) J. N. Cooper and S. E. King, Middle Atlantic Regional Meeting of the American Chemical Society, Wilkes-Barre, Pa., April 1974, Paper 239.
(7) J. Cooper, G. Staudt, M. Smalser, L. Settzo and G. Haight, *Inorg. Chem.*, **12**, 2075 (1973).
(8) L. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **77**, 5814 (1955).
(9) W. Reynolds and S. Fuksuhima, *Inorg. Chem.*, **2**, 176 (1963).
(10) The assistance of A. J. Zielen, Chemistry Division, Argonne National Laboratory, is gratefully acknowledged.
(11) Yu. Mikhailov, V. Kuznetsov, and E. Kovaleva, *Zh. Strukt. Khim.*, **9**, 710 (1968); *J. Struct. Chem. (Engl. Transl.)*, **9**, 620 (1968).
(12) E. Genser and R. Connick, *J. Chem. Phys.* **58**, 990 (1973).
(13) J. A. Effenberger, *Diss. Abstr.*, **22**, 749 (1961).